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Denudation Rates of the Hawaiian Islands by Rivers and Groundwaters[1]

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ABSTRACT: The carbonic acid produced by the microbial oxidation of organic matter is the most important chemical weathering agent of the Hawaiian basaltic rocks. The total denudation rate of the Hawaiian Islands ranges from 11 to 50 mg/cm^2/yr (or 0.04–0.19 mm/yr). The island of Hawaii has the lowest denudation rate among the Hawaiian Islands.

BASED ON THE REMOVAL RATE of dissolved calcium by rivers, Moberly (1963) estimated the total denudation rate (including both chemical and physical) of the Kaneohe Bay watershed on the island of Oahu, Hawaii, to be about 34 mg/cm^2/yr or 0.13 mm/yr (based on a density of basaltic rocks in the area of 2.6 g/cm^3). Since the denudation rate of any river drainage area is a complex function of rainfall rate, river runoff, vegetation coverage, texture and composition of parental rocks, etc. (Garrels and Mackenzie 1971, Sherman and Ikawa 1968), this paper addresses the question of how comparable Moberly's estimated value is to other areas in the Hawaiian island chain. The specific purposes of the present paper are to demonstrate (1) what factors control the chemical compositions of rivers and groundwaters in the Hawaiian Islands, and (2) how the chemical and physical denudation rates in the Hawaiian Islands vary as functions of various environmental factors. The extensive water resources data base collected by the U.S. Geological Survey annual report from 1975 to 1984 is the basis for this work.

CHEMICAL COMPOSITION OF RIVERS AND GROUNDWATERS

In general, the dissolved concentrations of major ions, [M], in rivers decrease and the suspended particle concentrations increase when the river runoff (F_w, in cubic feet per second) increases. Figure 1 shows these relationships for water samples from the Wailuku River at Hilo on the island of Hawaii (USGS Station No. 16213000, monthly data from October 1979 to September 1981). One exception is sulfate concentration data, which are quite variable and show no direct correlation with runoff. Another interesting observation is the near constancy or only slight decrease of chloride ion concentration as the runoff increases. The chloride ion in rain and river waters is supplied mainly by the sea-salt aerosols from the ocean. The $[SO_4^{2-}]/[Cl^-]$ weight ratio in rainwater along Saddle Road, which is almost parallel to Wailuku River, ranges from 0.20 near seashore to 0.86 inland at an elevation of 1625 m (Eriksson 1957). The average is about 0.4 as compared to 0.14 for seawater, probably indicating an excess source of dimethylsulfide (DMS), which is released to the atmosphere at the air–sea interface and oxidized to SO_2 and sulfate (Bates and Cline 1985). Other possible sources of the excess sulfate are the anthropogenic inputs from the continents and local volcanic gases. The volcanic input is, however, relatively small (Harding and Miller 1982). With an average chloride concentration of about 5–6 mg/liter in the Wailuku River water, the sulfate contribution from rainwater should be about 2–2.4 mg/liter in river water. The observed $[SO_4^{2-}]$ of most samples of Wailuku River water are, however, much less than 2–2.4 mg/liter, indicating a high degree of sorption of sulfate by soils (Hasan et al. 1970).

The concentrations of dissolved organic carbon, organic nitrogen, inorganic nitrogen, and phosphate in the same water samples are also quite variable, and again show no relationship to the runoff (Figure 2). Apparently, the direct source of these dissolved nutrients

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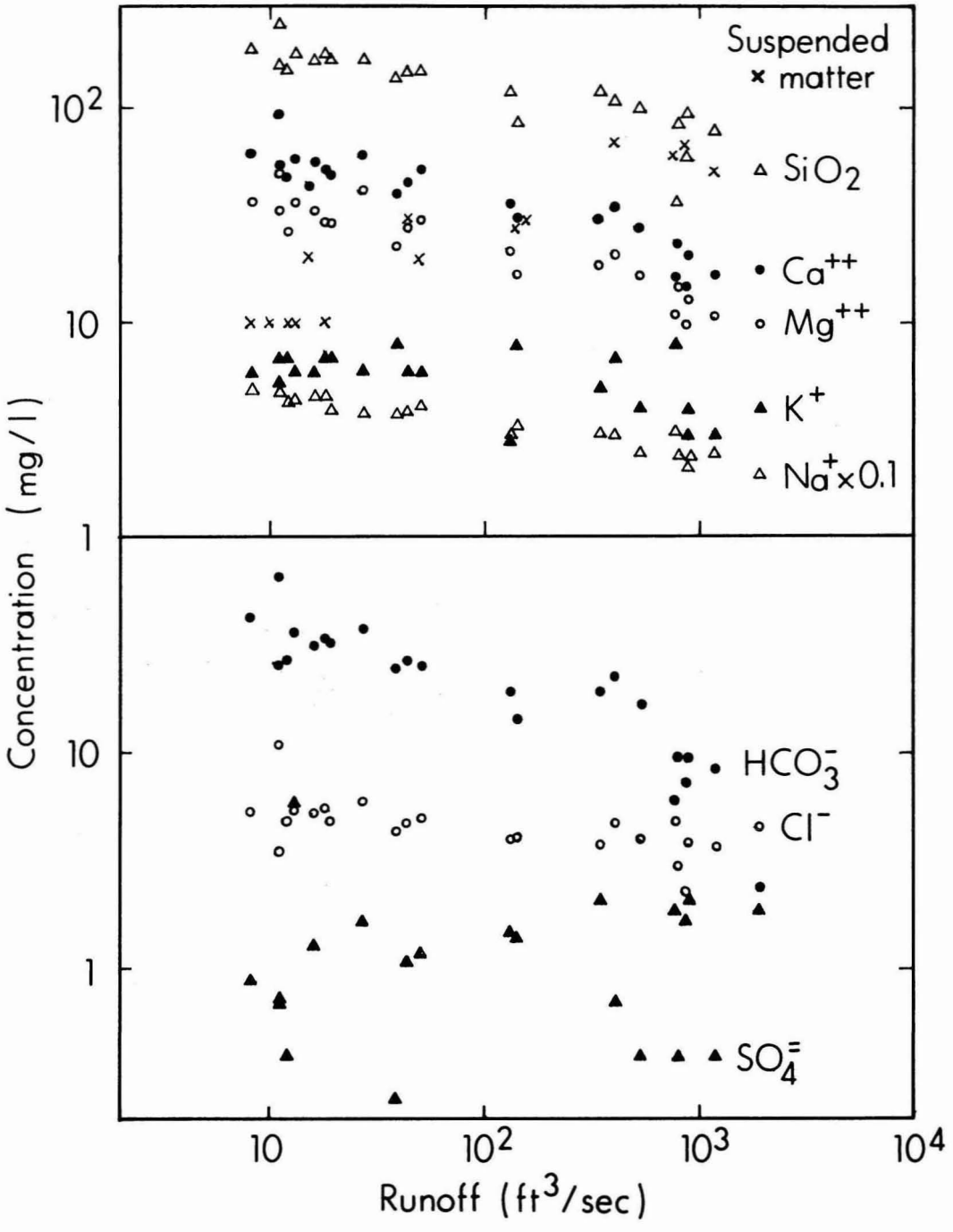

FIGURE 3. The concentrations (after subtracting sea-salt contributions) of major cations and dissolved SiO_2 plotted against bicarbonate ion concentration in rivers and groundwaters of Hawaii and Kauai islands.

is mainly the organic matter accumulated in the soils and some from fertilizers used on the sugarcane in the watershed, rather than the weathering of basaltic rocks.

The relationships between the concentrations of bicarbonate and major cations as well as dissolved SiO_2 after subtracting the sea-salt contributions are shown in Figure 3 for water samples from the Wailuku River at Hilo (USGS Station No. 16213000), Waimea River at Waimea on the island of Kauai (USGS Station No. 16031000, October 1979–September 1981), and groundwater samples around the islands of Hawaii and Kauai (October 1972–September 1975). The locations where these water samples were taken are shown in Figures 4 and 8. The sea-salt contributions were estimated by $([M]/[Cl^-])_{seawater} \times [Cl^-]_{sample}$, where [M] is the concentration of any particular ion. The concentrations of Mg^{2+}, Ca^{2+}, Na^+, and K^+ are more or less linearly related to that of bicarbonate (slope of near 1 in Figure 3; the greater scatter for Na^+ and K^+ is in part caused by large sea-salt corrections), even though river and groundwater samples were taken in different years and localities. The SiO_2 concentration does not increase as fast as $[HCO_3^-]$ (slope of less than 1 in Figure 3). Also, $[SiO_2]$ in groundwaters tends to be higher than in rivers of similar $[HCO_3^-]$ (Figure 3). This difference may be partly explained by the uptake of silicon by the surface vegetation (Fox et al. 1967).

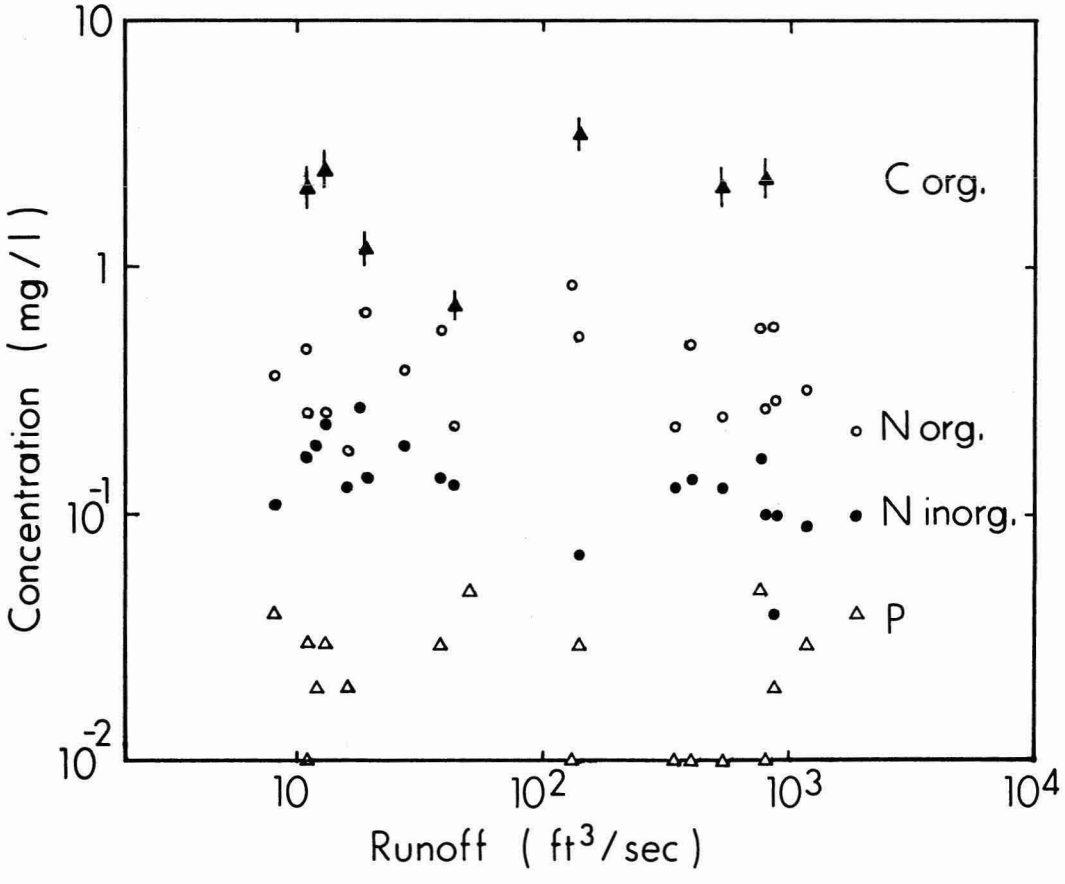

FIGURE 2. The concentrations of dissolved nutrients in the Wailuku River at Hilo as a function of runoff (October 1979–September 1981).

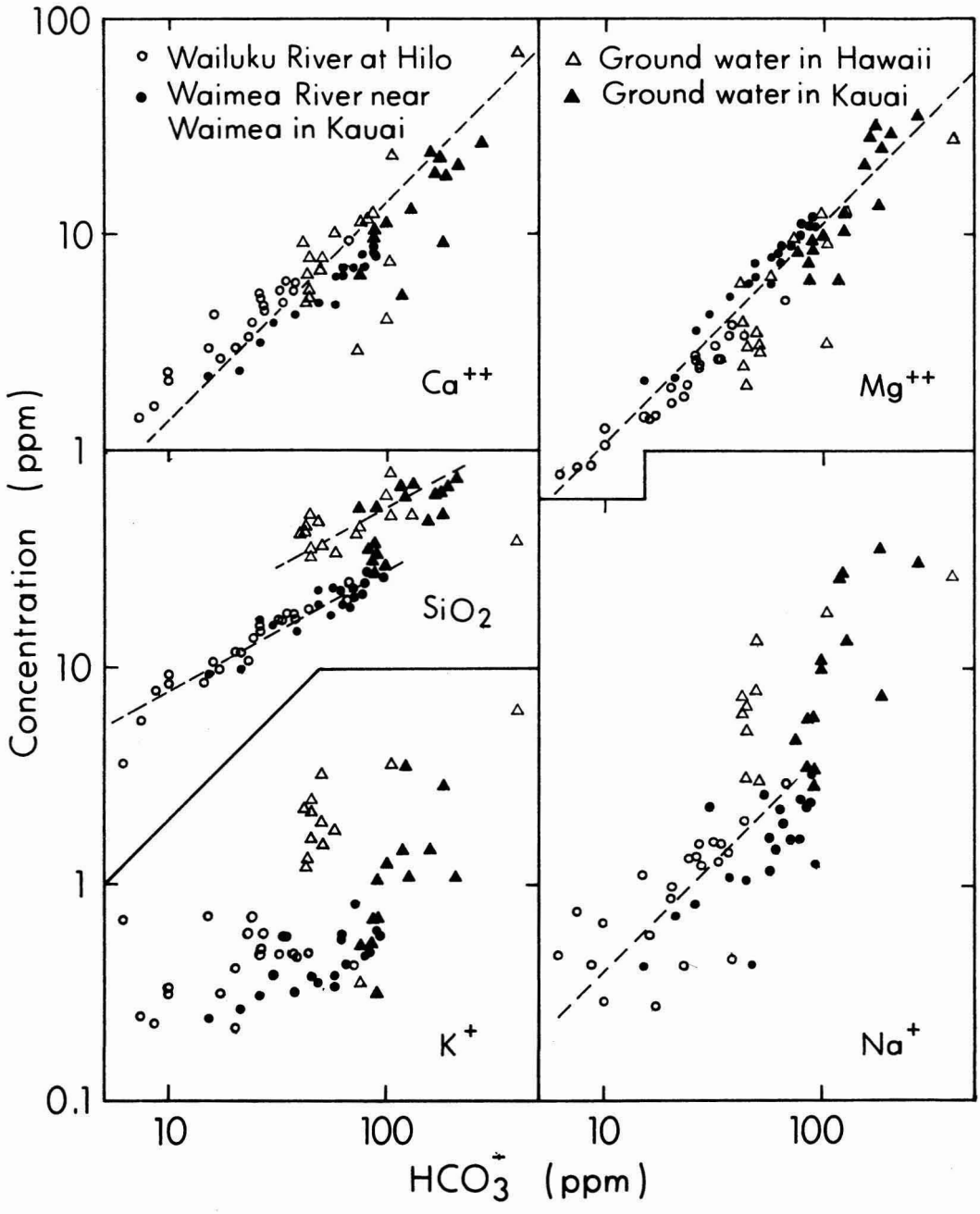

FIGURE 3. The concentrations (after subtracting sea-salt contributions) of major cations and dissolved SiO_2 plotted against bicarbonate ion concentration in rivers and groundwaters of Hawaii and Kauai islands.

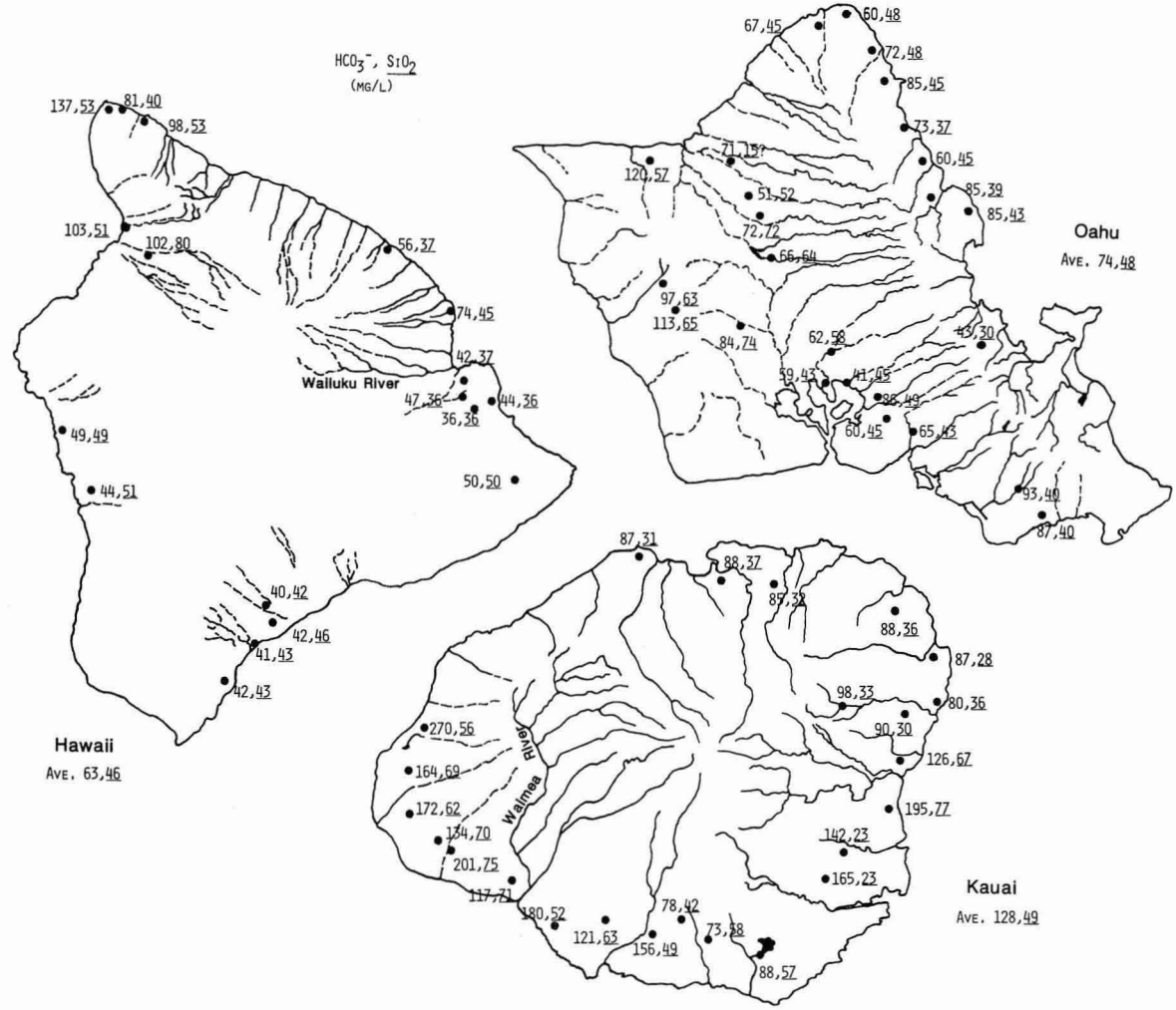

FIGURE 4. The concentrations of bicarbonate and silica (underlined) in the groundwaters of Hawaii, Oahu, and Kauai islands.

Except for coral reefs and caprocks along the shorelines, carbonate rocks are rare on the Hawaiian Islands. Therefore, the main source of bicarbonate in Hawaiian rivers and groundwaters must be carbonic acid produced by microbial oxidation of organic matter in the soil columns and root respiration. The high partial pressure of CO_2, and thus carbonic acid, in soils is well documented (Buyanovsky and Wagner 1983, Jong and Schappert 1972, Keller 1986, Yamaguchi et al. 1967). The direct incorporation of atmospheric CO_2 into soil via rainfall at pH less than 5 is negligible. The abundance of organic matter, root system, and microbial activities in soils are, in turn, closely related to vegetation coverage and rainfall rate. The high $[Mg^{2+}]$ and the linear correlation between $[Mg^{2+}]$ and $[HCO_3^-]$ (Figure 3) also do not indicate the dissolution of carbonate rocks [no dolomite on islands; the atmospheric dust inputs of calcite and dolomite from the Asian continent are negligibly small (Ferguson 1970)] as the main source of bicarbonate, Mg^{2+}, and Ca^{2+}. The light $\delta^{13}C$ values of dissolved inorganic carbon in both rivers and groundwaters on Oahu [mostly within the range of $-18 \pm 2‰$ (Hufen 1974)] further support this conclusion.

After the sea-salt correction, the positive charge of major cations in river and groundwater samples is mostly balanced by bicarbonate anion (Figure 3). Therefore, the hydrogen ion of carbonic acid should be the major chemical weathering agent that interacts with basaltic rocks to produce secondary minerals, dissolved cations, bicarbonate, and silica in natural waters (e.g., Garrels and Mackenzie 1971, Li 1972). The hydrogen ion contribution from rainwater with pH of around 4.5–5 in the Hawaiian Islands (Dugan and Ekern 1984, Eriksson 1957, Miller and Yoshinaga 1981) is relatively minor except in active volcanic areas on the island of Hawaii where the pH of rainwater can be locally as low as 3–4 (Harding and Miller 1982). Organic acids in soil do contribute some hydrogen ion, but they are eventually oxidized to carbonic acid by microorganisms during the percolation of water down the soil column (Cronan and Aiken 1985).

The relative mobility of elements during the weathering of parental rocks can be expressed by the partition ratio K_d = concentration of an element in solid divided by that in solution after sea-salt correction. The higher the K_d, the lower the mobility of an element. One example is shown in Table 1 for the average alkaline series basalts on the island of Hawaii (Basaltic Volcanism Study Project 1981) and the sea-salt corrected chemical composition of Wailuku River water at Hilo (USGS Station No. 16713000, March 1981, when the runoff rate is similar to the long-term average). According to the relative magnitude of K_d's in Table 1, the sequence of relative mobility is $Ca > K > Na \approx Mg > Ba \approx Si \simeq P \gg Mn \approx Fe$, which is similar to that given by Colman (1982) based on the composition changes in weathering rings of basalts and andesites. One exception is that the mobility of K obtained by Colman falls between Si and Fe. As mentioned earlier, the concentration of silica in the Hawaiian groundwaters is always higher than in rivers at a comparable $[HCO_3^-]$ (Figure 3). Therefore, the mobility of Si in groundwater becomes very similar to that of Mg.

The partial pressure of CO_2 (P_{CO_2}, in atmospheres), pH, and activity of bicarbonate ($a_{HCO_3^-}$) are related by the following equation:

$$\text{pH} = -\log K_{CO_2} \times K_1 \times P_{CO_2} + \log a_{HCO_3^-} \quad (1)$$

TABLE 1

THE PARTITION RATIOS (K_d) OF ELEMENTS BETWEEN ALKALINE SERIES BASALTS (BASALT VOLCANISM STUDY PROJECT 1981) AND THE WAILUKU RIVER WATERS ON THE ISLAND OF HAWAII

	BASALTS (%)	RIVER (mg/l)	K_d ($\times 10^4$ ml/g)
Si	23.7	4.1	5.8
Fe	8.8	0.12	73
Mg	3.9	1.4	2.8
Ca	5.6	3.0	1.9
Na	3.1	1.1	2.8
K	1.4	0.7	2.1
Mn	0.16	0.002	80
P	0.20	0.03	6.7
Ba	0.04	0.007	5.7
Al	8.24	—	—

where $K_{CO_2} = a_{H_2CO_3}/(P_{CO_2} \times a_{H_2O}) = 10^{-1.47}$ and $K_1 = a_{H^+} \times a_{HCO_3^-}/a_{H_2CO_3} = 10^{-6.35}$ at 25°C. The relationship is shown as solid lines in Figure 5*A* [the values for K_{CO_2} and K_1 are taken from Drever (1982)]. The observed pH and $[HCO_3^-]$, which is approximately equal to $a_{HCO_3^-}$, for the water samples given in Figure 3 as well as samples from an upstream station of the Waimea River (USGS Station No. 16019000, October 1979–September 1981) are also plotted in Figure 5*A*. Except for a few data points, the P_{CO_2} in rivers and groundwaters is always much higher than the atmospheric P_{CO_2} ($\approx 10^{-3.5}$ atm), again suggesting the continuous input of carbonic acid by microbial oxidation of organic matter even in the subsurface groundwater reservoirs. The microbial activity in groundwater aquifers is well documented (e.g., Hirsch and Rades-Rohkohl 1983). The sources of organic matter in the Hawaiian groundwater aquifers should be the dissolved and fine particulate or colloidal organic matter carried down by the percolating waters.

If a parcel of natural water is in equilibrium with calcite, then

$$\log(a_{Ca^{2+}}/a_{H^+}) = \log(K_{sp}/K_2) - \log a_{HCO_3^-} \qquad (2)$$

where $K_{sp} = a_{Ca^{2+}} \times a_{CO_3^{2-}} = 10^{-8.34}$ and $K_2 = a_{H^+} \times a_{CO_3^{2-}}/a_{HCO_3^-} = 10^{-10.33}$. The relationship given in equation (2) is shown as a solid line in Figure 5*B*. [The values for K_{sp} and K_2 are from Drever (1982).] The observed $a_{Ca^{2+}}/a_{H^+}$ and $a_{HCO_3^-}$ for various samples (no sea-salt corrections) are also plotted in the same figure, where it can be seen that the waters are steadily approaching saturation with respect to calcite from upstream to downstream and in groundwater reservoirs.

The plots of chemical data from the same set of samples (no sea-salt corrections) on various activity–activity phase diagrams (taken from Drever 1982), as shown in Figure 6, indicate that the stable secondary minerals after weathering of basalts should be gibbsite in upstream, kaolinite in downstream, and various smectites and/or feldspar in the groundwaters. This prediction is in agreement with the observation that the weathered materials from several 60-ft wells on the island of Oahu consist mainly of gibbsite and halloysite/kaolinite in the top 25 ft and smectite with variable amounts of pedogenic feldspar below 30 ft (Jones 1986). Sherman (1952) also demonstrated that the composition of minerals in Hawaiian soils changes systematically from gibbsite and goethite to kaolinites, then smectites, as the average rainfall decreases.

CHEMICAL AND PHYSICAL DENUDATION RATES

The daily discharge rates of dissolved (F_d) and particulate (F_p) matter by the river at any sampling station are estimated by

$$F_d = F_w \times ([Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+] + [SiO_2])$$
$$F_p = F_w \times C_p$$

where F_w = daily runoff of the river at the station (usually given in cubic feet per second, but can be converted to liters per day by multiplying by 2447×10^3); C_p = river suspended particle concentration (in milligrams per liter); and [M]'s = concentrations (after sea-salt corrections) of major dissolved species (in milligrams per liter). For the estimate of F_d, the $[HCO_3^-]$ is excluded, since the source for bicarbonate is the organic matter in soils rather than basaltic rocks, as mentioned earlier. The F_d and F_p data as a function of F_w for the Wailuku River at Hilo are shown in Figure 7 as an example. The values for F_p were obtained from daily F_w and C_p data for the period between October 1980 and September 1981. The F_d values were obtained from biweekly chemical data for the period between October 1979 and September 1981. The F_d rate increases more or less linearly with F_w up to about 10^3 ft^3/sec. In other words, the dissolution rate of basalts is directly proportional to runoff or rainfall in a watershed. At the higher F_w, however, the rate of change of F_d decreases gradually. In contrast, the F_p increase is a power function of F_w, as also shown by Ekern (1976) and Doty et al. (1981). At lower F_w, the F_d is dominant over F_p.

The average daily discharge rates of dissolved matter ($\bar{F}_d$) as obtained by calculating $(1/n) \times \sum F_d$ for n observations and by reading off the F_d at $\bar{F}_w = (1/n) \times \sum F_w$ in the cali-

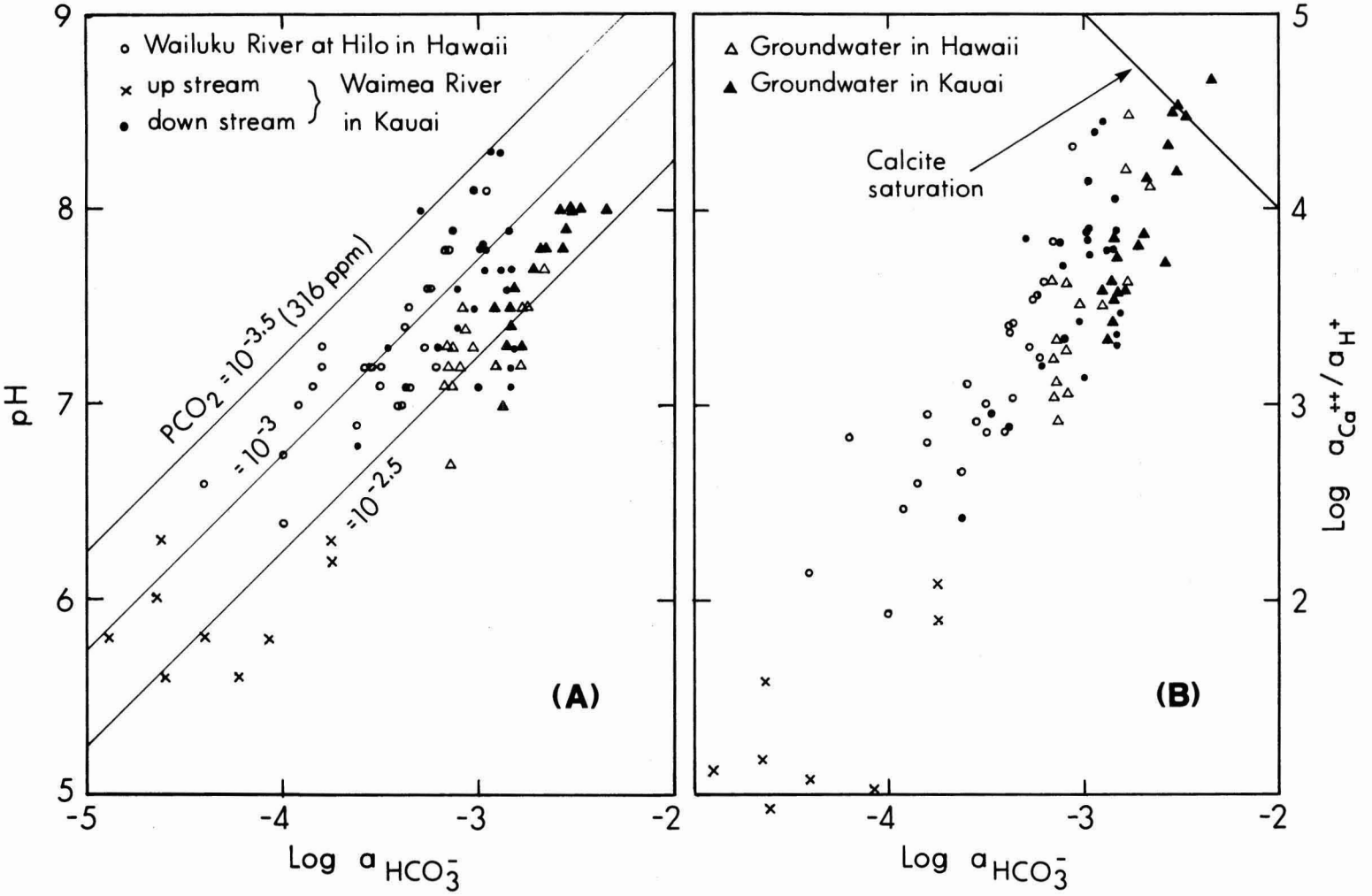

FIGURE 5. (*A*) Log $a_{HCO_3^-}$ plotted against pH and (*B*) log $a_{HCO_3^-}$ plotted against log $a_{Ca^{2+}}/a_{H^+}$ for rivers and groundwaters in Hawaii and Kauai.

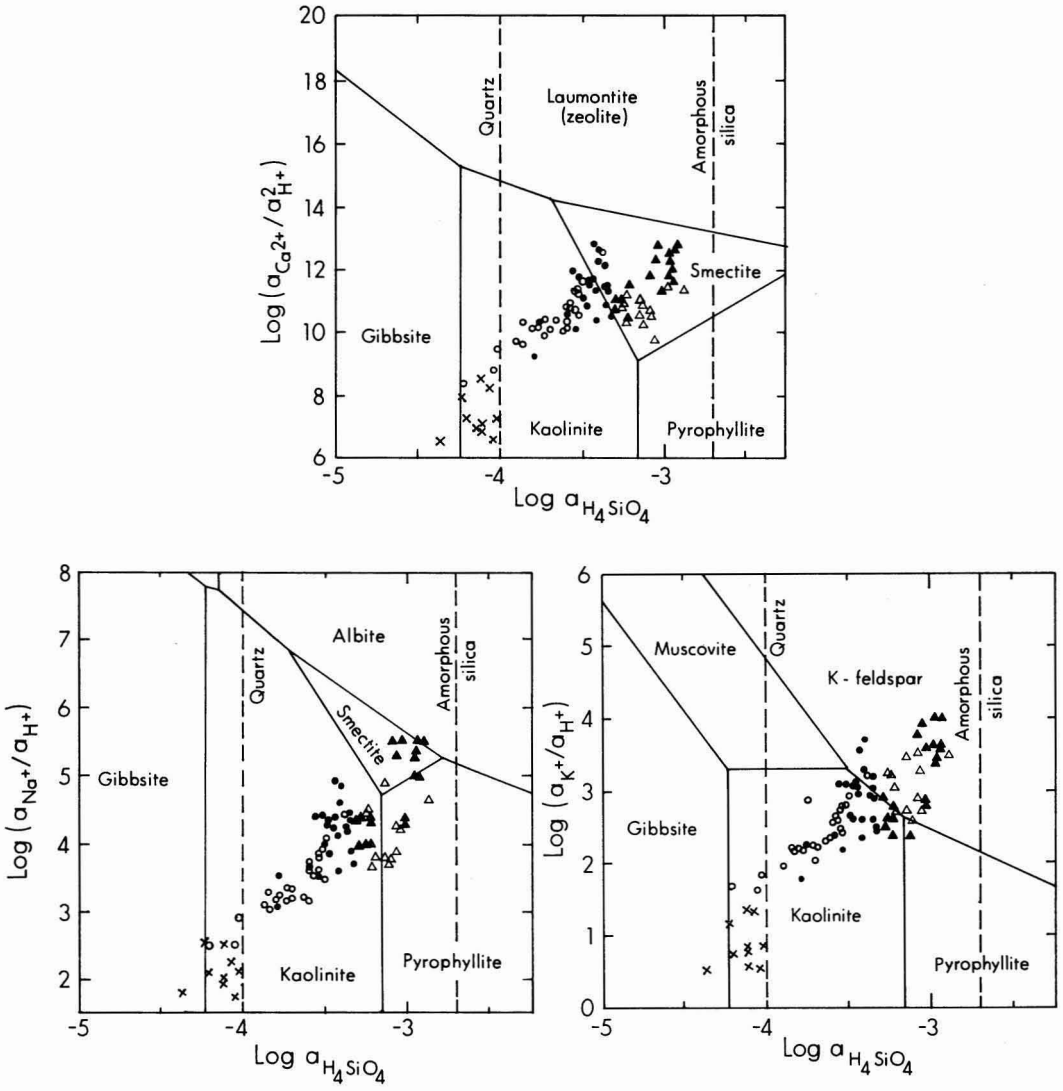

FIGURE 6. The log activity–log activity ratio plots of rivers and groundwaters from Hawaii and Kauai islands (the symbols are the same as in Figure 5), and the stability fields of various secondary minerals given by Drever (1982).

bration curve (dashed line in Figure 7) are very similar (as one would have expected, because F_d is more or less linearly correlated to F_w except at high F_w). Therefore, if one can establish the calibration curve for F_d versus F_w at any hydrographic station, then the $\bar{F}_d$ can be roughly estimated by using $\bar{F}_w$ obtained for long periods of time (at least more than 10 years). Once $\bar{F}_d$ is known, the average chemical denudation rate (CDR) of any river drainage area (A) upstream can be calculated by multiplying $365 \times \bar{F}_d/A$. The CDR calculation results for three Hawaiian islands are shown in Figure 8.

In general, the CDR is higher on the windward (northeast) than on the leeward side of each island. This observation is consistent with the fact that the windward side of each island has higher rainfall, thus also generally denser vegetation and higher carbonic acid

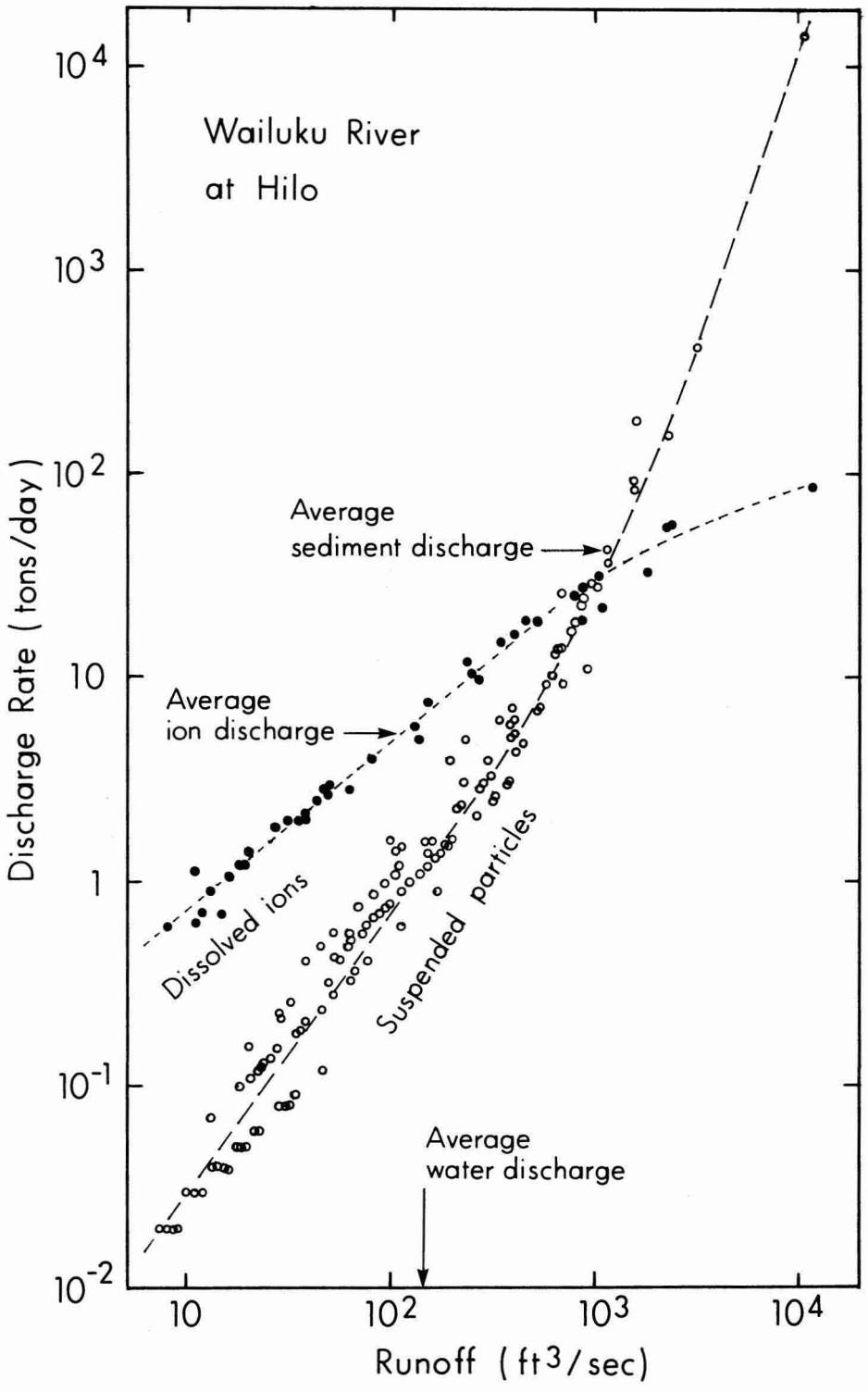

FIGURE 7. The daily discharge rates of dissolved chemical species and suspended particles as a function of river runoff in the Wailuku River at Hilo.

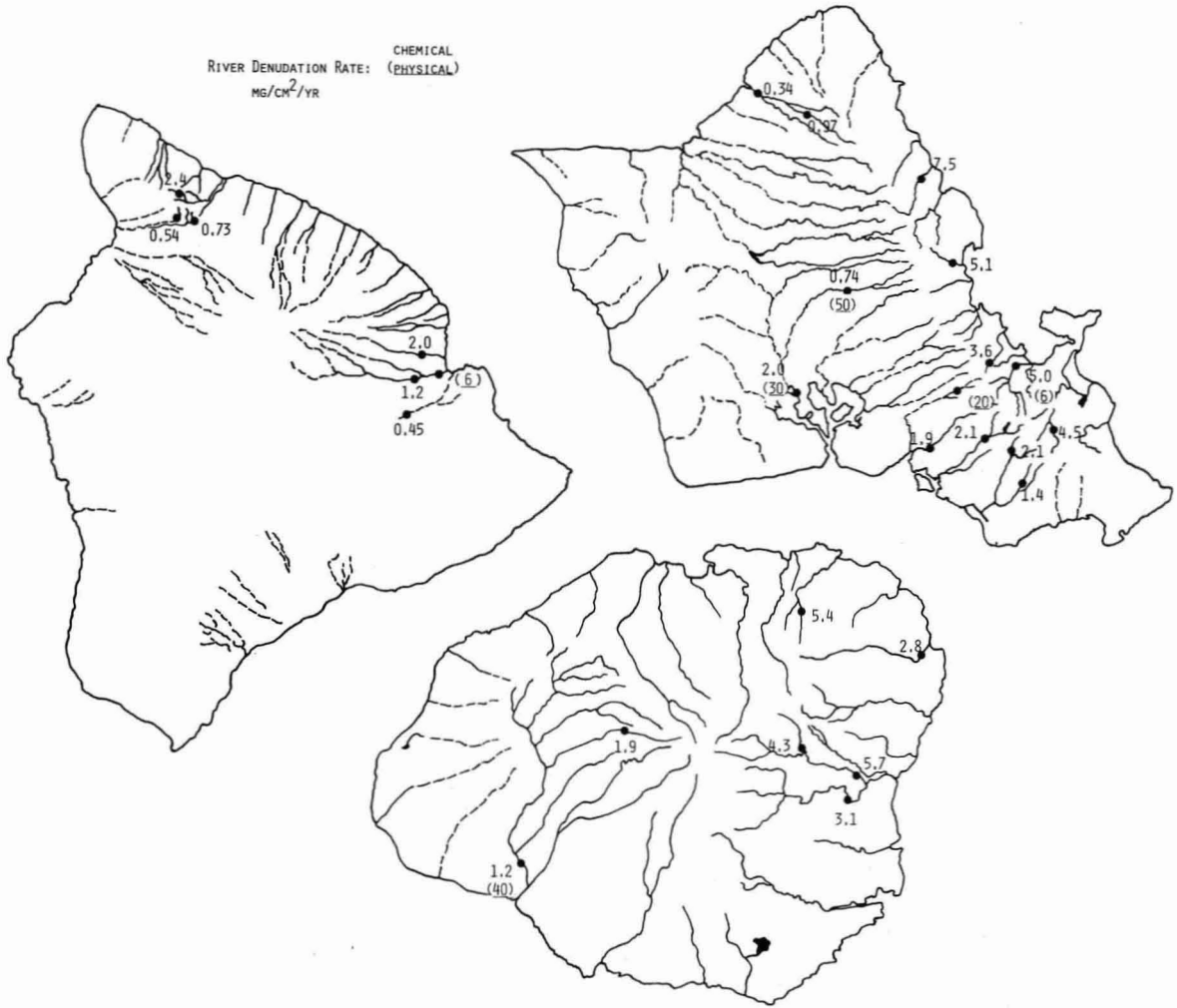

FIGURE 8. The chemical and physical (in parentheses) denudation rates of river drainages on three Hawaiian islands.

production than the leeward side. Comparison of the CDR on the windward sides of these three islands shows that it is lowest on the island of Hawaii, probably reflecting the high surface area of relatively young basaltic rocks free of or low in vegetation and humus coverage on this island.

Only a few river stations provide daily records on C_p for more than several years since 1972. For those stations, I chose the F_w and C_p data in a year when the annual water discharge rate was close to its long-term average (more than 10 years) to calculate the average daily discharge rate of suspended particles, $\bar{F}_p = (1/365)\sum(C_p \times F_w)$. The average physical denudation rate (PDR) of a watershed is then defined by $365 \times \bar{F}_p/A$. The PDR results are shown in Figure 8 (numbers in parentheses). For the Waikele River on Oahu and the Waimea River on Kauai, however, there are no extensive daily data on C_p. Therefore, all the F_p data from several years were plotted against F_w in a diagram similar to Figure 7 to obtain the calibration curve first. Then I again chose the daily F_w data from a year when the annual water discharge rate was close to its long-term average to obtain daily F_p values from the calibration curve and then to calculate $\bar{F}_p$ and the PDR. This procedure may have an uncertainty of 50% because, as shown in Figure 7, the $\bar{F}_p$ is very sensitive to a few large $\bar{F}_p$ values at the high end of F_w. Doty et al. (1981) also summarized the $\bar{F}_p$ values over a 5-year period on the island of Oahu, based on the USGS data. The PDR data are too few to make any generalization except that the PDR of the Wailuku River watershed is again the lowest among the three islands.

Assuming a steady state, the groundwater recharge and discharge rates in the Hawaiian Islands should be equal. Therefore, the average chemical denudation rate of an island by groundwaters can be calculated by the summation of average concentrations of major dissolved species in groundwater (with proper sea-salt correction) multiplied by the islandwide groundwater recharge rate and divided by the total area of the island. The islandwide groundwater recharge rate and the total area of each island are given by Macdonald et al. (1983). The chemical compositions of groundwaters between 1972 and 1975 are summarized in the USGS Water Resources Data 1975. Interestingly, the islandwide average CDRs by groundwaters among the three islands are very similar, and their magnitudes are comparable to those for rivers (Table 2).

Table 2 summarizes the CDR by groundwaters and the possible ranges of CDR and PDR by rivers, along with the total denudation rates (chemical and physical) in three Hawaiian islands. A CDR of 1 mg/cm^2/yr corresponds to a leaching rate of about 0.2 mg Ca/cm^2/yr for river water and 0.13 mg Ca/cm^2/yr for groundwater. On the other hand, the Ca content in average Hawaiian basaltic rocks is about 6.4 $\pm$ 0.5% (or 9 $\pm$ 1% CaO; Basaltic Volcanism Study Project 1981). Therefore, from the total CDR (rivers + groundwater), one can estimate the mass of fresh basaltic rocks that would interact annually with waters to lose all their Ca and most of their Mg, Na, K, and SiO_2 contents in dissolved form and their residual solid, probably as river suspended particles. These results are also shown in Table 2. Interestingly, these estimates fall nicely within the ranges of the total denudation rates obtained from the "ob-

TABLE 2

SUMMARY OF DENUDATION RATES (mg/cm^2/yr) IN THREE HAWAIIAN ISLANDS

	Hawaii	Oahu	Kauai
Chemical (C = R + G)	4.7–6.8	5.1–11.9	4.9–9.4
River (R)	0.5–2.4	0.7–7.5	1.2–5.7
Groundwater (G)	4.2	4.4	3.7
Physical (P)	6	6–30	?–40 $\pm$ 20
Total (P + C)	11–13	11–42	?–49 $\pm$ 20
Total calculated from Ca leaching rate	11–16	11–32	11–26

served" PDR and CDR. The finding is consistent with the suggestion that the formation processes of Hawaiian amphitheater-headed valleys consist of repeated cycles of a soil formation period through chemical weathering and subsequent soil avalanching or mass wasting (Scott and Street 1976).

The Waimea Canyon on the island of Kauai is as deep as 1000 m. The average erosion depth is about 500 m in the Waimea River watershed since the eruption of Makaweli lava ($3.5–4.05 \times 10^6$ yr ago; Macdonald et al. 1983). Therefore, the average total denudation rate of the Waimea watershed is about 0.13 ± 0.02 mm/yr or 34 ± 5 mg/cm^2/yr, which is in good agreement with that estimated from the present CDR and PDR (49 ± 20 mg/cm^2/yr, Table 2), and is by chance equal to that of the Kaneohe Bay watershed given by Moberly (1963).

The average chemical denudation rates of the North and South American, Asian, African, and European continents is 3 ± 1 mg/cm^2/yr (Garrels and Mackenzie 1971), as compared to 5–12 mg/cm^2/yr in the Hawaiian Islands. The latter values are comparable to those for the carbonaceous rocks in southern China (8–12 mg/cm^2/yr; Li et al. 1984), where the karst topography is world famous.

CONCLUSIONS

1. The hydrogen ion of carbonic acid, which is produced by microbial oxidation of organic matter, is the major chemical weathering agent of basaltic rocks in the Hawaiian Islands.
2. After correcting for the sea-salt contribution, the charge of major cations in the Hawaiian rivers and groundwater is balanced mainly by bicarbonate anion.
3. The majority of Hawaiian waters are undersaturated with respect to calcite but steadily approaching saturation from upstream to downstream and groundwater reservoirs.
4. The stable or metastable alteration products of primary rock weathering are gibbsite upstream, kaolinite downstream, and smectites and K-feldspar in groundwater.
5. The relative mobility of elements during the weathering of Hawaiian basaltic rocks is roughly in the order of $Ca > K > Na \approx Mg > Ba \approx Si \simeq P \gg Mn \approx Fe$.
6. The discharge rate of dissolved matter is always higher than that of particulate matter in the Hawaiian rivers when the river runoff is relatively low. The former increases more or less linearly and the latter exponentially with increasing river runoff.
7. The chemical denudation rate by rivers is always higher on the wet windward side than the dry leeward side of the Hawaiian Islands.
8. The chemical denudation rates by groundwaters among the Hawaiian Islands are very similar, and their magnitudes are comparable to those by rivers.
9. The total denudation rate of the Hawaiian Islands ranges from 11 to 50 mg/cm^2/yr. Moberly's estimate for Kaneohe Bay falls nicely within the range. The island of Hawaii tends to have the lowest rate.

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